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(54) Method of preparing silicone oil-in-water microemulsions

(57) Methods of forming microemulsions are disclosed which involve mixing an oil and water with a surfactant (S1) and a co-surfactant (S2). The oil, preferably a cyclic siloxane, is added to a solution of the surfactant (S1) and water. A two-phase system containing the siloxane results. The two-phase system is then titrated with co-surfactant (S2) until a clear isotropic microemulsion results. An emulsion polymerization catalyst is added to the clear isotropic microemulsion and polymerization of the cyclic siloxane is initiated. The polymerization is allowed to advance until the reaction is complete or a desired degree of polymerization (DP) has been obtained. Microemulsions of high molecular weight silicone polymers with low polydispersity are produced.

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Description

[0001] Our invention provides thermodynamically stable, clear, single phase, silicone oil-in-water microemulsions. These optically clear one phase microemulsions are useful in many personal care applications, especially as deodorant or skin care lotions and for delivering lipid soluble perfumes. In addition, the microemulsions can be used as a source

5 of very small, i.e., below 10 nanometer (nm), droplets of silicone oil, for use in textile finishing and as an additive in a hair conditioning product such as a shampoo. They also provide an alternative to the more volatile types of solvents typically used for diluting silicone oils. Because they exist as a single phase, the microemulsions are much easier to process.

10 [0002] Emulsions, especially silicone emulsions, are often opaque, cloudy and tend to separate on standing, as shown in U.S. Patents 4,999,398 and US 5,817,714. Microemulsions, in contrast, are desirable because they are thermodynamically stable and contain equilibrium microstructures that are smaller than typical emulsion droplets. Thus, microemulsion products are usually indefinitely stable and can be optically clear.

15 [0003] As used herein, the term emulsion or macroemulsion means a mixture of one immiscible liquid in another, in the form of droplets, with diameters approximately in the range of 100-1,000 nanometer (0.1-1.0 micrometer/1,000-10,000 angstrom Å). In contrast, a microemulsion means a single or one phase transparent, thermodynamically stable, mixture of two or more immiscible liquids and one or more surfactant(s) and co-surfactant(s).

20 [0004] The term microemulsion has been used loosely in the literature to describe any transparent composition containing water, oil and a surfactant, including compositions which are transparent by virtue of a very small structure size and index of refraction matching.

[0005] However, it is almost always apparent from the details of the preparation given, which type of composition is in fact being made, considering the order of addition of the components, their polymerization or when high energy mixing is involved.

25 [0006] Microemulsions, on the other hand, are generally always clear or transparent because they contain structures smaller than the wavelength of visible light, typically of the order of magnitude of 500 nanometer. Furthermore, a microemulsion, as that term is used herein, contains structures that are spontaneously self-assembled aggregates consisting of oil and surfactant monolayers or water and surfactant monolayers.

30 [0007] Although there are distinct domains present which are composed of water and oil, these types of systems can be properly described as being in the form of one phase, because the domains consist of molecular aggregates that spontaneously self-assemble.

[0008] A microemulsion may contain oil droplets dispersed in water (O/W), water droplets dispersed in oil (W/O) or it may be in the form of a bicontinuous structure or other structure. It is recognized by several inherent characteristics which are (i) that it contains oil, water and a surfactant; (ii) there is a high concentration of surfactant relative to oil; (iii) the system is optically clear; (iv) the phases do not separate by centrifugation; and (v) the system forms spontaneously.

35 [0009] For purposes of our invention, therefore, an emulsion is considered as containing structures having an average diameter of more than 100 nanometer (0.1 micrometer/1,000 angstrom Å), whereas a microemulsion contains structures having an average diameter of less than 100 nanometer (0.1 micrometer/1,000 angstrom Å), preferably less than 50 nanometer (0.05 micrometer/500 angstrom Å), and most preferably less than 10 nanometer (0.01 micrometer/100 angstrom Å). Microemulsion containing structures having an average diameter of as small as 5 nanometer

40 (0.005 micrometer/50 angstrom Å) is also contemplated herein.

[0010] Clarity or transparency is controlled to a great extent by the structure size of the dispersed phase. The scattering of light is dependent on the structure size. Therefore, clear or transparent compositions, according to this invention, are generally a single phase without droplets or structures when viewed with the naked eye.

45 [0011] Furthermore, while emulsions are recognized as inherently unstable systems separating with time, microemulsions according to our invention can be formed spontaneously and are generally stable indefinitely.

[0012] True microemulsions of cyclic siloxanes in water are quite rare. Yet, classical methods of microemulsion formation have been known for many years in which a non-polar organic oil, water, a surfactant (S1) and a co-surfactant (S2) are mixed to form microemulsions, alleged to be thermodynamically stable. An adaptation of the classical method, coined the titration method, has even achieved some degree of notoriety in microemulsion circles, whereby organic oils, but not silicone oils, are added to a solution of a surfactant S1 and water to form two-phase mixtures. A co-surfactant (S2) is then slowly added with mixing, i.e., the titration, until the system becomes clear. It is said that microemulsions of particle size of 4 nanometer to 20 nanometer can be formed in this fashion.

50 [0013] Advantage is taken of a titration method in this invention, in order to facilitate arriving at the production of silicone oil-in-water microemulsions, which can contain high molecular weight silicone polymers, with structures so small that they appear invisible to the naked eye, as a practical matter.

55 [0014] Our invention provides microemulsions of polysiloxanes in water and to methods for their preparation. Silicone oil-in-water microemulsions are prepared via the following steps:

1. A primary surfactant is dissolved in water.
 2. A siloxane is added and a two-phase mixture is formed.
 3. With simple mixing, a co-surfactant is slowly added to the two-phase mixture until a clear isotropic microemulsion of a siloxane-in-water is formed. These systems typically have a mean particle size of less than 20 nanometer and a narrow particle size distribution.

[0015] Siloxanes can, for example, be added to solutions containing ionic surfactants, such as dodecytrimethyl ammonium bromide (DTAB) and sodium dodecyl sulfate (SDS), until a two-phase system is formed. A co-surfactant, such as 1-pentanol, is then titrated into the solution, until a clear, isotropic microemulsion results. Salts such as sodium chloride can also be included.

[0016] The system can be polymerized by the addition of a strong acid or a strong base ring-opening polymerization catalyst or a condensation polymerization catalyst. The use of such a thermodynamically stable pre-emulsion leads to a vastly simplified polymerization process. Some benefits include fast polymerization rates and high molecular weights. In some instances, a very low molecular weight polydispersity has been observed.

[0017] Our invention, therefore, provides a method of making a thermodynamically stable, clear, single phase, silicone oil-in-water microemulsion, by (i) forming a two-phase mixture obtained by combining water, a siloxane and a non-ionic surfactant, a cationic surfactant or an anionic surfactant; (ii) adding to the two-phase mixture a co-surfactant selected from monohydroxy alcohols, diols and triols, until a thermodynamically stable, clear, single phase, pre-microemulsion containing the siloxane is formed; (iii) adding a polymerization initiator to the thermodynamically stable, clear, single phase, pre-microemulsion; (iv) heating the thermodynamically stable, clear, single phase, pre-microemulsion; (v) agitating the heated, thermodynamically stable, clear, single phase, pre-microemulsion; and (vi) allowing the siloxane to polymerize, until a thermodynamically stable, clear, single phase, microemulsion is formed containing a higher molecular weight silicone polymer.

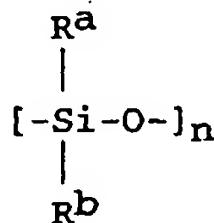
[0018] The invention also provides a method of making a thermodynamically stable, clear, single phase, silicone oil-in-water microemulsion, by (i) forming a two-phase mixture obtained by combining water, a siloxane and a nonionic surfactant, a cationic surfactant or an anionic surfactant; and (ii) adding to the two-phase mixture a co-surfactant such as a monohydroxy alcohol, diol or triol, until a thermodynamically stable, clear, single phase, microemulsion containing the siloxane is formed.

[0019] Emulsion polymerization methods for making emulsions of high viscosity polymers start with low viscosity polymer precursors, i.e., monomers or reactive oligomers, which are immiscible in water; a surfactant to stabilize polymer precursor droplets in water; and a water soluble polymerization catalyst.

[0020] Typically, the catalyst is a strong mineral acid such as hydrochloric acid or a strong alkaline catalyst such as sodium hydroxide. These components are added to water, the mixture is stirred and polymerization is allowed to advance until the reaction is complete or the desired degree of polymerization (DP) is reached and an emulsion of the polymer is formed.

[0021] One example of such an emulsion polymerization process is described in U.S. Patent 2,891,920 which shows a method of making aqueous emulsions of polydimethylsiloxanes, starting with precursor molecules of a polydimethylsiloxane.

[0022] Polydiorganosiloxane precursors generally used in such processes include cyclic siloxanes which are relatively insoluble in water and which can be polymerized using an emulsion polymerization technique. These cyclic siloxanes generally are species having the formula:



in which R^a and R^b denote methyl, ethyl, propyl, vinyl, allyl or phenyl groups; and n is 3, 4, 5 or 6.

[0023] The cyclic siloxane precursors can be pure species, such as octamethylcyclotetrasiloxane, hexamethylcyclotrisiloxane, decamethylcyclopentasiloxane, tetramethyltetravinylcyclotetrasiloxane and tetramethyltetraphenylcyclotetrasiloxane or mixtures of the species can be used. One example of a mixture is a combination of cyclopolydimethylsiloxanes having three, four and five siloxane units.

[0024] The reaction medium can include small portions of other organosilicon compounds containing hydrolyzable or silanol groups in the molecule which are capable of polymerization. Some examples include amine functional silanes, vinyl functional silanes and halogen-alkyl functional silanes. Silanes most often used include N-(2-aminoethyl)-3-(ami-

nopropyltrimethoxysilane, vinyltriethoxysilane, vinyltriacetoxysilane and 3-chloropropyltrimethoxysilane.

[0025] The reaction medium generally comprises water, an effective amount of surfactant to stabilize polydiorganosiloxane droplets formed in the medium and an effective amount of an initiator to polymerize the polydiorganosiloxane precursor.

5 [0026] According to the present invention, the emulsion polymerization process is utilized in preparing clear, stable, microemulsions, from an otherwise thermodynamically stable pre-emulsion which is formed with the aid of certain surfactant(s) S1 and co-surfactant(s) S2.

10 [0027] Thus, compositions according to this invention can be prepared by combining and preferably contain 1-50 percent by weight of a silicone oil component; 50-98 percent by weight of water; 5-50 percent by weight of a surfactant or combination of surfactants S1; 5-15 percent by weight of a co-surfactant or combination of co-surfactants S2; optionally 0.01-1.0 percent by weight of a polymerization catalyst; and a sufficient quantity of neutralizing agent, including an excess of as much as 50 percent, necessary to neutralize the catalyst.

15 [0028] The silicone oil component of the composition can be a cyclic siloxane having the formula $\{R^1 R^2 SiO\}_x$ in which R^1 and R^2 are alkyl groups having 1-6 carbon atoms, aryl groups such as phenyl or alkenyl groups such as vinyl and allyl and x is 3-6. The silicone oil component of the composition can also be a short chain linear siloxane having the formula $R^c_3 SiO \{R^d_2 SiO\}_y SiR^c_3$ or the formula $HOR^c_2 SiO \{R^d_2 SiO\}_y SiR^c_2 OH$ in which R^c and R^d are alkyl groups having 1-6 carbon atoms or aryl groups such as phenyl and y is 0-10.

20 [0029] Some suitable cyclic siloxanes are hexamethylcyclotrisiloxane (D_3), a solid with a boiling point of 134°C. and the formula $\{(Me_2SiO\}_3$; octamethylcyclo-tetrasiloxane (D_4) with a boiling point of 176°C., a viscosity of 2.3 mm²/s and the formula $\{(Me_2SiO\}_4$; decamethylcyclopentasiloxane (D_5) with a boiling point of 210°C., a viscosity of 3.87 mm²/s and the formula $\{(Me_2SiO\}_5$; dodecamethylcyclohexasiloxane (D_6) with a boiling point of 245°C., a viscosity of 6.62 mm²/s and the formula $\{(Me_2SiO\}_6$; and 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane with the formula $\{(Me)(CH_2=CH)SiO\}_4$.

25 [0030] Some suitable short chain linear siloxanes are hexanethyldisiloxane (MM) with a boiling point of 100°C., viscosity of 0.65 mm²/s and formula $Me_3SiOSiMe_3$; octamethyltrisiloxane (MDM) with a boiling point of 152°C., viscosity of 1.04 mm²/s and formula $Me_3SiOMe_2SiOSiMe_3$; decamethyltetrasiloxane (MD₂M) with a boiling point of 194°C., viscosity of 1.53 mm²/s and formula $Me_3SiO(Me_2SiO)_2SiMe_3$; dodecamethylpentasiloxane (MD₃M) with a boiling point of 229°C., viscosity of 2.06 mm²/s and formula $Me_3SiO(Me_2SiO)_3SiMe_3$; tetradecamethyl-hexasiloxane (MD₄M) with a boiling point of 245°C., viscosity of 2.63 mm²/s and formula $Me_3SiO(Me_2SiO)_4SiMe_3$; hexadecamethylheptasiloxane (MD₅M) with a boiling point of 270°C., viscosity of 3.24 mm²/s and formula $Me_3SiO(Me_2SiO)_5SiMe_3$; and a silanol fluid with the formula $HO\{(CH_3)_2SiO\}_6H$. In these formulas, Me is used to represent a methyl group -CH₃.

30 [0031] The composition may contain a nonionic surfactant which should be a non-silicon atom containing nonionic emulsifier. Most preferred are alcohol ethoxylates $R^3-(OCH_2CH_2)_aOH$, most particularly fatty alcohol ethoxylates. Fatty alcohol ethoxylates typically contain the characteristic group -(OCH₂CH₂)_aOH which is attached to fatty hydrocarbon residue R^3 which contains eight to twenty carbon atoms, such as lauryl (C₁₂), cetyl (C₁₆) and stearyl (C₁₈). While the value of "a" may range from 1 to 100, its value is typically in the range of 12 to 40.

35 [0032] Some examples of suitable nonionic surfactants are polyoxyethylene (4) lauryl ether, polyoxyethylene (5) lauryl ether, polyoxyethylene (23) lauryl ether, polyoxyethylene (2) cetyl ether, polyoxyethylene (10) cetyl ether, polyoxyethylene (20) cetyl ether, polyoxyethylene (2) stearyl ether, polyoxyethylene (10) stearyl ether, polyoxyethylene (20) stearyl ether, polyoxyethylene (21) stearyl ether, polyoxyethylene (100) stearyl ether, polyoxyethylene (2) oleyl ether and polyoxyethylene (10) oleyl ether. These and other fatty alcohol ethoxylates are commercially available under trademarks and tradenames such as ALFONIC®, BRIJ, GENAPOL®, NEODOL®, SURFONIC® and TRYCOL.

40 [0033] The composition may also contain a cationic surfactant. Cationic surfactants useful in the invention include compounds containing quaternary ammonium hydrophilic moieties in the molecule which are positively charged, such as quaternary ammonium salts represented by $R'R''R'''N^+X^-$ where R' , R'' , R''' and R'''' are alkyl groups containing 1-30 carbon atoms or alkyl groups derived from tallow, coconut oil or soy; and X is halogen, i.e., chlorine or bromine. Most preferred are dialkyldimethyl ammonium salts represented by $R'R''N^+(CH_3)_2X^-$ where R' and R'' are alkyl groups containing 12-30 carbon atoms or alkyl groups derived from tallow, coconut oil or soy; and X is halogen. Monoalkyltrimethyl ammonium salts can also be employed and are represented by $R'N^+(CH_3)_3X^-$ where R' is an alkyl group containing 12-30 carbon atoms or an alkyl group derived from tallow, coconut oil or soy; and X is halogen.

45 [0034] Representative quaternary ammonium salts are dodecytrimethyl ammonium bromide (DTAB), didodecyldimethyl ammonium bromide, dihexadecyldimethyl ammonium chloride, dihexadecyldimethyl ammonium bromide, dioctadecyldimethyl ammonium chloride, dieicosyldimethyl ammonium chloride, didocosyldimethyl ammonium chloride, dicoconutdimethyl ammonium chloride, ditallowdimethyl ammonium chloride and ditallowdimethyl ammonium bromide. These and other quaternary ammonium salts are commercially available under tradenames such as ADOGEN, ARQUAD, TOMAH and VARIQUAT.

50 [0035] The composition may also contain an anionic surfactant. Examples of anionic surfactants include sulfonic acids and their salt derivatives; alkali metal sulfosuccinates; sulfonated glyceryl esters of fatty acids such as sulfonated

monoglycerides of coconut oil acids; salts of sulfonated monovalent alcohol esters such as sodium oleyl isothionate; amides of amino sulfonic acids such as the sodium salt of oleyl methyl tauride; sulfonated products of fatty acid nitriles such as palmitonitrile sulfonate; sulfonated aromatic hydrocarbons such as sodium alpha-naphthalene monosulfonate; condensation products of naphthalene sulfonic acids with formaldehyde; sodium octahydro anthracene sulfonate; alkali metal alkyl sulfates such as sodium lauryl (dodecyl) sulfate (SDS); ether sulfates having alkyl groups of eight or more carbon atoms and alkylaryl sulfonates having one or more alkyl groups of eight or more carbon atoms.

[0036] Commercial anionic surfactants useful in this invention include triethanolamine linear alkyl sulfonate sold under the tradename BIO-SOFT N-300 by the Stepan Company, Northfield, Illinois; sulfates sold under the tradename POLYSTEP by the Stepan Company; and sodium n-hexadecyl diphenyloxide disulfonate sold under the tradename DOWFAX 8390 by The Dow Chemical Company, Midland, Michigan.

[0037] The composition contains a co-surfactant which may be a compound such as a monohydroxy alcohol, a diol or a triol. Some preferred co-surfactants include 1-butanol, 1-pentanol, 1-decanol, 1-hexadecanol, ethylene glycol, propylene glycol, trimethylene glycol and glycerol. Most preferred are the C₄ and C₅ alcohols for preparing fluid-type micro-emulsions, while the C₆ to C₁₀ alcohols are useful for preparing microemulsion gels.

[0038] If desired, the composition may contain an electrolyte such as sodium chloride or ammonium chloride, to increase the viscosity of the final product.

[0039] Catalysts capable of polymerizing siloxanes in the presence of water can be used in this invention. They include those materials generally known as condensation polymerization catalysts capable of cleaving siloxane bonds. Representative condensation polymerization catalysts include, but are not limited to, strong acids such as substituted benzenesulfonic acids, aliphatic sulfonic acids, hydrochloric acid and sulfuric acid; and strong bases such as quaternary ammonium hydroxides and metal hydroxides such as sodium hydroxide.

[0040] Condensation catalysts, which under certain conditions do not readily cleave siloxane bonds, can also be used in conjunction with siloxane precursors having a structure generally corresponding to HO[(CH₃)₂SiO)]_zH where z generally has a value of 1 to 30. Some examples of condensation catalysts of this type include weak organic acids and weak organic bases or combinations thereof, such as blends of carboxylic acids and organic amines.

[0041] The method of stopping the reaction includes neutralization of the catalyst by addition of equal or slightly greater stoichiometric amounts of an acid or base, depending upon the type of catalyst. Strong or weak acids/bases may be used to neutralize the reaction. However, care must be taken when using a strong acid/base not to over neutralize as it is possible to re-catalyze the reaction. It is preferred to neutralize with sufficient quantities of acids or bases so that the microemulsion has a pH of less than 7 when a cationic surfactant is present and a pH of greater than 7 when an anionic surfactant is present. Representative neutralizing agents are phosphoric acid, glacial acetic acid and triethanolamine.

[0042] The purpose of the following examples is to illustrate the invention in more detail.

35 Example 1

[0043] This example describes a general procedure used to prepare a number of microemulsions according to the method of the present invention. Conditions used in preparing each microemulsion according to the general procedure and the characteristics of the resulting microemulsions of Examples 2-10 are summarized in accompanying Table 1.

[0044] The siloxane used in these examples was octamethylcyclotetrasiloxane (D₄). The cationic surfactant was dodecytrimethyl ammonium bromide (DTAB) CH₃(CH₂)₁₁N⁺(CH₃)₃Br⁻. The anionic surfactant was sodium dodecyl sulfate (SDS), i.e., sodium lauryl sulfate CH₃(CH₂)₁₁OSO₃⁻Na⁺. The nonionic surfactant was an ethoxylated alcohol R³-(OCH₂CH₂)_aOH where R³ was C₁₂H₂₅ and a was 5. It is abbreviated and shown in Table 1 as C₁₂E₅. The co-surfactants were primary amyl alcohol, i.e., 1-pentanol CH₃(CH₂)₄OH and cetyl alcohol, i.e., 1-hexadecanol C₁₆H₃₃OH.

[0045] According to the general procedure, the siloxane, a cationic surfactant, an anionic surfactant or a nonionic surfactant were added to a 20 milliliter glass vial, after the weight of each of the ingredients had been recorded using an analytical balance. A TEFLO[®] coated stirring bar was placed in the vial and the vial was closed with a lid. The vial was placed onto a stirring plate. The co-surfactant was titrated into the vial dropwise, with mixing, until a thermodynamically stable, single phase, clear, pre-microemulsion had formed at room temperature, i.e., 20-25°C.

[0046] At this point, the contents of the vial were transferred to a glass reaction vessel, where polymerization of the siloxane was catalyzed by adding to the vessel either a 50 percent by weight aqueous sodium hydroxide catalyst solution or a 35 percent by weight aqueous hydrochloric acid catalyst solution, depending upon the nature of the surfactant. Generally, acid catalysts were used with anionic surfactants, alkaline catalysts were used with cationic surfactants and acid or alkaline catalysts were used with nonionic surfactants. While other combinations do exist, they are considered less preferred.

[0047] The temperature of the reaction vessel was adjusted to 50°C. Generally, addition of the catalyst to the clear microemulsion in the vessel causes the contents of the vessel to become cloudy. However, the reaction in the vessel was allowed to proceed to completion, whereupon the contents of the reaction vessel was neutralized with glacial acetic

acid or triethanolamine.

[0048] The silicone polymer was recovered from the microemulsion by breaking the product using a salt. The silicone polymer was isolated and analyzed by Gel Permeation Chromatography (GPC). In the extraction procedure, 1.5 gram of anhydrous calcium chloride was added to a four ounce French square bottle, followed by 10 gram of the emulsion product to be broken. To the bottle was added 20 milliliter of methanol and 25 milliliter of n-pentane. The bottle was shaken and the top was unscrewed slowly to release any pressure in the bottle. The mixture was transferred to a 50 milliliter plastic centrifuge tube and spun for 10-15 minutes at 3000 rpm (314 radian per second). Some of the procedures may require longer periods of time in the centrifuge for separation of the layers. The top n-pentane layer containing the silicone polymer was then removed with a pipette and transferred to a vial for analysis by GPC.

[0049] This otherwise standard emulsion salt break technique was modified to the extent that, instead of the n-pentane layer being pipetted into an aluminum pan to dry, the n-pentane layer was pipetted into a vial to assure that any volatile siloxane species contained in the n-pentane layer did not evaporate prior to analysis of the sample via GPC.

[0050] In the accompanying Table 1, alpha (α) was used to indicate the weight percent of the siloxane oil + the weight percent of the siloxane oil + the weight percent of water. Gamma (γ) indicates the weight percent of the cationic, anionic or nonionic surfactant S1 + the weight percent of the co-surfactant S2 + the weight percent of the siloxane oil + the weight percent of water + the weight percent of the cationic, anionic or nonionic surfactant S1 + the weight percent of the co-surfactant S2.

[0051] The data in Table 1 is based upon preparations of compositions having a total mass of ten gram, unless otherwise indicated. In Examples 3 and 7, the polymerization reaction was conducted in stages at two temperatures as noted in Table 1, i.e., the reaction medium was first heated to 70°C. and then it was cooled to 40°C.

[0052] The silicone polymer was characterized and is shown in Table 1, by its polydispersity DP_n and DP_w . In this regard, it is noted that the molecular weights of silicone fluids with a viscosity less than 5 mm²/s at 25°C. are generally quite precise, since such fluids are generally fractionally distilled products and relatively pure molecular species. Above 5 mm²/s, however, molecular weights are average values (i.e., M_w), since the fluids are residue products and therefore contain a distribution of molecular sizes.

[0053] The molecular weight distribution of a polymeric sample describes the relative numbers of molecules of all molecular weight values. Averages of molecular weight such as the number average molecular weight M_n , the weight average molecular weight M_w and the Z-average molecular weight M_z are parameters most commonly used to describe the general shape of the molecular weight distribution. A peak weight-average molecular weight M_w or M_p is another parameter commonly used. One convenient measure of molecular weight distribution in a polymer is the ratio of its weight average molecular weight M_w to its number average molecular weight M_n , i.e., M_w/M_n or the polydispersity of the polymer. Generally, for perfectly uniform monodisperse polymers, the ratio is one.

[0054] Methods for measuring molecular weight distribution and molecular weight averages for silicones are the same as for other polymers. Gel Permeation Chromatography (GPC), sometimes termed size exclusion chromatography, is the most common, convenient and useful method. This technique is based on separation of polymer molecules in a column packed with porous cross-linked gels, typically polystyrene, according to their size in solution.

[0055] Thus, when a polymer solution is eluted, species of higher molecular weight which permeate the porous polystyrene gel to a lesser degree than species of lower molecular weight, pass through the column more rapidly and hence are eluted first. The system is calibrated and yields an estimated molecular weight distribution for a given sample. The only requirements are that the sample is soluble and stable in a suitable solvent and that the sample components can be detected in the eluent by some means.

[0056] The system is calibrated by injecting dilute solutions of narrow dispersity standards of a known molecular weight. The retention volume or retention time of each standard is then plotted against the log molecular weight of the standard and fitted to an equation for a curve. The molecular weight distribution values of a given polymer are then calculated and expressed as relative to that standard.

[0057] Polydispersity can be expressed in terms of DP_n and DP_w rather than M_n and M_w and this terminology has been used in Table 1. DP is the degree of polymerization in the silicone polymer which indicates by way of example, a number "n" of repeating units in polymer species of the types HO(Me₂SiO)_nH or HOMe₂SiO(Me₂SiO)_nSiMe₂OH where Me is methyl.

[0058] Data for polydispersity of the silicone polymer in the microemulsion of Example 2 is not shown in Table 1. The data could not be obtained using standard extraction procedures indicating the stability of the microemulsion of Example 2.

[0059] Silicone polymers in the single phase compositions according to this invention most preferably have average droplet diameters of less than 50 nanometer to provide optical clarity. The criteria used to determine clarity and the term Clear in Table 1 is whether text can be read with the naked eye through a two centimeter diameter bottle filled with the microemulsion. This is a viable means of determining clarity as noted in Microemulsions Theory and Practice, Edited by Leon M. Prince, Academic Press, Inc., Pages 7-10, New York (1977), wherein the author states "Visual recognition of microemulsions should not be taken lightly. In fact, the microemulsion chemist should train himself carefully in this

art. Use of sunlight rather than an artificial source of light is recommended. The eye is better than a microscope, because the limit of resolution of a light microscope in blue light is only about $0.1 \mu\text{m}$, so that droplets smaller than $0.14 \mu\text{m}$ cannot be seen".

5

TABLE 1

EXAMPLE	S1	S2	α	γ	Particle Size, μm	Appearance
2	SDS	$\text{C}_5\text{H}_{11}\text{OH}$	0.053	0.19	0.0050	Clear
3	SDS	$\text{C}_5\text{H}_{11}\text{OH}$	0.053	0.19	0.0050	Clear
4	SDS	$\text{C}_5\text{H}_{11}\text{OH}$	0.060	0.27		Clear
5	DTAB	$\text{C}_5\text{H}_{11}\text{OH}$	0.100	0.27	0.0061	Clear
6	DTAB	$\text{C}_5\text{H}_{11}\text{OH}$	0.220	0.37	0.0046	Clear
7	SDS	$\text{C}_5\text{H}_{11}\text{OH}$	0.400	0.29	0.0289	Clear
8	DTAB	$\text{C}_5\text{H}_{11}\text{OH}$	0.050	0.27	0.0043	
9	SDS	$\text{C}_5\text{H}_{11}\text{OH}$	0.050	0.17	0.0102	
10	DTAB	$\text{C}_{16}\text{H}_{33}\text{OH}$	0.050	0.24		
11	C12E5	$\text{C}_5\text{H}_{11}\text{OH}$	0.100	0.24	0.0151	Clear
EXAMPLE	Catalyst	Reaction Temp. $^{\circ}\text{C}$	DP_n	DP_w	Polydispersity	
2	HCl	50				
3	HCl	70/40	21.0	320	1.510	
4	NaOH	50	25.0	37.0	1.464	
5	NaOH	50	33.0	57.0	1.725	
6	NaOH	50	103.0	122.0	1.188	
7	HCl	70/40	15.8	20.3	1.286	
8						
9						
10						
11	NaOH	22	34.0	54.0	1.605	

[0060] Following the general procedure described in Example 1, some additional examples were carried out, for the purpose of illustrating the versatility of the invention, in the use of other types of alcohols and other types of siloxanes. Examples 12-21 are summarized in Table 2.

[0061] The silanol used in Example 12 was a siloxane with a structure corresponding to $\text{HO}(\text{CH}_3)_2\text{SiO}_6\text{H}$. The siloxane used in Example 13 was cyclic siloxane species 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane which has a structure corresponding to $\{(\text{CH}_3)(\text{CH}_2=\text{CH})\text{SiO}\}_4$.

[0062] Example 17 is comparative and this is beyond the scope of the present invention. Its purpose is to show that alcohols having less than about four carbon atoms are not suitable for use as co-surfactants. As noted previously, the preferred co-surfactants according to the invention are the C_4 and C_5 alcohols for the preparation of fluid-type microemulsions and C_6 to C_{10} alcohols for preparing microemulsion gels. Generally, any alcohol containing 4 to 16 carbon atoms can be used. Example 21 shows that a salt such as sodium chloride can be included and that its presence is not deleterious.

TABLE 2

EX.	S1	S2	α	γ	Siloxane	Particle Size, μm	Appearance
12	SDS	$\text{C}_5\text{H}_{11}\text{OH}$	0.027	0.13	Silanol		Clear

TABLE 2 (continued)

EX.	S1	S2	α	γ	Siloxane	Particle Size, μm	Appearance	
5	13	SDS	C ₅ H ₁₁ OH	0.050	0.17	MeVi Cyclic	0.0440	Clear
	14	SDS	C ₅ H ₁₁ OH	0.050	0.17	MD ₂ M	0.0118	Clear
	15	DTAB	C ₅ H ₁₁ OH	0.060	0.27	D ₅	0.0066	Clear
	16	DTAB	C ₄ H ₉ OH	0.130	0.38	D ₅	0.0099	Clear
10	17	SDS	C ₃ H ₇ OH	0.050	0.54	D ₄	5.2550	Clear
	18	SDS	C ₄ H ₉ OH	0.050	0.25	D ₄	0.0131	Clear
	19	SDS	C ₆ H ₁₃ OH	0.050	0.20	D ₄		Clear Gel
	20	SDS	C ₈ H ₁₇ OH	0.050	0.14	D ₄		Foamy Gel
15	21	DTAB NaCl	C ₅ H ₁₁ OH	0.100	0.21	D ₄	0.0100	Clear

[0063] These single phase clear microemulsions have value in the personal care industry. It can be used alone or blended with other cosmetic fluids, to form a variety of over-the-counter (OTC) personal care products.

[0064] Thus, our microemulsions are useful in antiperspirants and deodorants since it leaves a dry feel. They are lubricious and improve the properties of skin creams, skin care lotions, moisturizers, facial treatments such as acne or wrinkle removers, personal and facial cleansers, bath oils, perfumes, colognes, sachets, sunscreens, pre-shave and after-shave lotions, shaving soaps and shaving lathers. They can be used in hair shampoos, hair conditioners, hair sprays, mousses, permanents, depilatories and cuticle coats, to enhance gloss and provide conditioning benefits. In cosmetics, they function as a leveling and spreading agent for pigments in make-ups, color cosmetics, foundations, blushes, lipsticks, eyeliners, mascaras, oil removers, color cosmetic removers and powders. They are also useful as a delivery system for oil and water-soluble substances such as vitamins. When incorporated into sticks, gels, lotions, aerosols and roll-ons, the composition imparts a dry, silky-smooth, payout.

[0065] In addition, because these clear one phase microemulsions exhibit a variety of advantageous and beneficial properties such as (i) clarity, (ii) very small structure size, (iii) ultra-low interfacial tensions, (iv) the ability to combine properties of water and oil in a single homogeneous fluid, (v) shelf stability, and (vi) ease of preparation; they can have wide applications in other industrial areas such as textile finishing.

Claims

1. A method of making a thermodynamically stable, clear, single phase, silicone oil-in-water microemulsion, comprising the steps of (i) forming a two-phase mixture comprising water, a siloxane and a nonionic surfactant, a cationic surfactant or an anionic surfactant; (ii) adding to the two-phase mixture a co-surfactant selected from monohydroxy alcohols, diols and triols, until a thermodynamically stable, clear, single phase, pre-microemulsion containing the siloxane is formed; (iii) adding a polymerization initiator to the thermodynamically stable, clear, single phase, pre-microemulsion; (iv) heating the thermodynamically stable, clear, single phase, pre-microemulsion; (v) agitating the heated, thermodynamically stable, clear, single phase, pre-microemulsion; and (vi) allowing the siloxane to polymerize, until a thermodynamically stable, clear, single phase, microemulsion is formed containing a silicone polymer.
2. A method according to claim 1 in which the co-surfactant is selected from the group consisting of 1-butanol, 1-pentanol, 1-decanol, 1-hexadecanol, ethylene glycol, propylene glycol, trimethylene glycol and glycerol.
3. A method of making a thermodynamically stable, clear, single phase, silicone oil-in-water microemulsion, comprising the steps of (i) forming a two-phase mixture comprising water, a linear or cyclic siloxane and a nonionic surfactant, a cationic surfactant or an anionic surfactant; and (ii) adding to the two-phase mixture a co-surfactant selected from the group consisting of monohydroxy alcohols, diols and triols, until a thermodynamically stable, clear, single phase, microemulsion containing the siloxane is formed.
4. A microemulsion prepared according to the methods of claims 1 or 3.